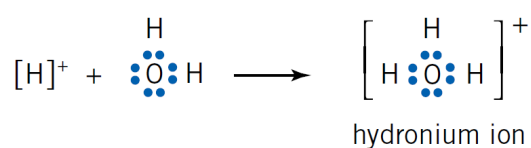


Theories of Acids and Bases

Arrhenius' Theory

- Acids:

- Arrhenius proposed that an acid is a substance that **ionises** in an aqueous solution to produce hydrogen ions
- E.g. $\text{HCl}_{(g)} \rightarrow \text{H}^+_{(aq)} + \text{Cl}^-_{(aq)}$
- Hydrogen ions (H^+) produced in aqueous solution are sometimes represented as hydronium ions (H_3O^+)
 - As the proton's charge is located in such a small volume, the attraction between a polar water molecule and a proton is greater than for other ions
 - The proton is in fact more likely to exist as a hydronium ion. This reaction is represented in the illustration below



- In the H_3O^+ ion, the H^+ has formed an ion-dipole attractive force with one of the lone pair of electrons on the oxygen atom of the water molecule

- Bases:

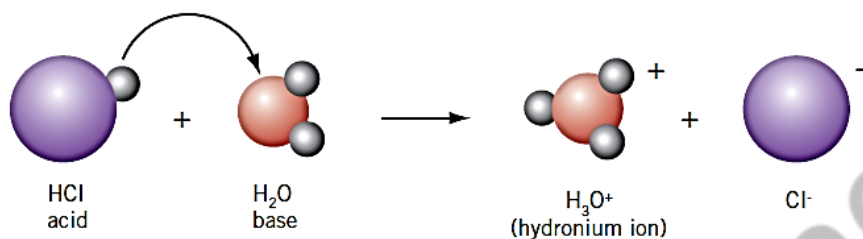
- Arrhenius proposed that a base is a substance that produces hydroxide ions in solution
 - E.g. Sodium hydroxide (NaOH), a soluble ionic solid, dissociates in water to form sodium ions and hydroxide ions
 - $\text{NaOH}_{(s)} \rightarrow \text{Na}^+_{(aq)} + \text{OH}^-_{(aq)}$

- Neutralisation

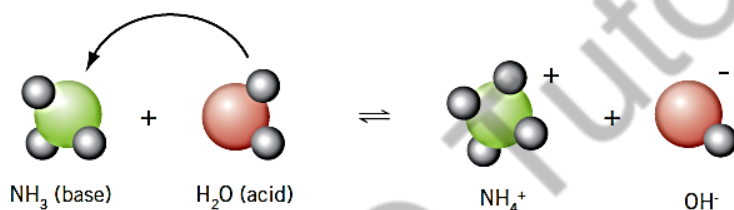
- In the Arrhenius model, hydrogen ions are responsible for the properties of acids and hydroxide ions are responsible for the properties of bases
- In the neutralisation reaction between acids and bases, the acidic and basic properties of each (respectively) are also "neutralised" when these ions combine to form water:
 - $\text{H}^+_{(aq)} + \text{OH}^-_{(aq)} \rightarrow \text{H}_2\text{O}_{(l)}$

Brønsted-Lowry Theory

- A more general model of acids and bases was developed independently by Brønsted and Lowry
- In the Brønsted-Lowry theory, an acid-base reaction is one that involves the transfer of a proton from one species to another
 - o The substance that donates the proton is an acid
 - o The substance that accepts the proton is a base
- E.g. The ionisation of HCl is represented as: $\text{HCl}_{(g)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{H}_3\text{O}^+_{(aq)} + \text{Cl}^-_{(aq)}$
 - o The HCl is donating the proton, and is therefore acting as the acid
 - o The H_2O is accepting the proton, and is therefore classified as a base



- E.g. In the reaction of ammonia with water: $\text{NH}_3_{(aq)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{NH}_4^+_{(aq)} + \text{OH}^-_{(aq)}$
 - o The NH_3 is accepting the proton, and is therefore acting as the base
 - o The H_2O is donating the proton, and is therefore classified as an acid



- In the Brønsted-Lowry theory, many substances can react as acids or bases
 - o In the two examples above, water is acting as a base (in its reaction with HCl) and as an acid (in its reaction with NH_3)

- Conjugate acid-base pairs

- In the Brønsted-Lowry theory:
 - A base, after it has received a proton, has the potential to react as an acid (i.e. donate a proton)
 - Similarly, an acid, after it has donated a proton, has the potential to react as a base (i.e. accept a proton)
- E.g. In the reaction: $\text{CH}_3\text{COOH}_{(\text{aq})} + \text{OH}^{-}_{(\text{aq})} \rightleftharpoons \text{H}_2\text{O}_{(\text{l})} + \text{CH}_3\text{COO}^{-}_{(\text{aq})}$
 - The CH_3COOH is acting as an acid, and the H_2O is acting as a base
 - The $\text{CH}_3\text{COO}^{-}$ ion can (now) under certain conditions, accept a proton. E.g. In the reaction between hydrochloric acid and sodium ethanoate:

$$\text{CH}_3\text{COO}^{-}_{(\text{aq})} + \text{H}_3\text{O}^{+}_{(\text{aq})} \rightleftharpoons \text{CH}_3\text{COOH}_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})}$$
 - The $\text{CH}_3\text{COO}^{-}$ accepts a proton from the H_3O^{+} and is therefore acting as a base
 - The $\text{CH}_3\text{COOH}/\text{CH}_3\text{COO}^{-}$ pair is described as a conjugate acid-base pair
- E.g. The ammonium ion and ammonia, $\text{NH}_4^{+}/\text{NH}_3$, constitute another conjugate acid-base pair
- Conjugate pairs can be represented as HA/A^{-} . A table of conjugate acid-base pairs is shown in the table below

	Acid	Conjugate base	
Completely ionised in water	H_2SO_4 HCl HNO_3	HSO_4^{-} Cl^{-} NO_3^{-}	Negligible base strength
	H_3O^{+} HSO_4^{-} H_3PO_4 CH_3COOH H_2CO_3 NH_4^{+} HCO_3^{-} H_2O OH^{-}	H_2O SO_4^{2-} $\text{H}_2\text{PO}_4^{-}$ $\text{CH}_3\text{COO}^{-}$ HCO_3^{-} NH_3 CO_3^{2-} OH^{-} O^{2-}	
Negligible acid strength	Acid strength increases ↑	Base strength increases ↓	

- The table is arranged in order of decreasing acid strength (e.g. H_2SO_4 is a strong acid, CH_3COOH is a fairly weak acid and H_2O is a very weak acid)
- The stronger a particular acid is, the weaker will be its conjugate base (e.g. HSO_4^{-} is a very weak base, NH_3 is a fairly weak base and O^{2-} is a strong base)
 - This also means that if the relative strengths of two acids or bases are known, then the relative strengths of their conjugate pairs can be determined

Strengths of Acids and Bases

- The strength of an acid or base refers to its ability to ionise/dissociate in solution (i.e. its electrolytic strength)

Strong acids

- Strong acids are those that essentially completely ionise to produce hydrogen ions in aqueous solution
- E.g. In a solution of hydrochloric acid, virtually all the hydrogen chloride molecules ionise to form hydrogen and chloride ions
 - $\text{HCl}_{(g)} \rightarrow \text{H}^+_{(aq)} + \text{Cl}^-_{(aq)}$
 $\text{HCl}_{(g)} + \text{H}_2\text{O}_{(l)} \rightarrow \text{H}_3\text{O}^+_{(aq)} + \text{Cl}^-_{(aq)}$
 - Because the equilibrium strongly favours the formation of products, a single arrow is used, showing only the forward reaction occurs
 - Using the Brønsted-Lowry approach, HCl is a stronger acid (proton donor) than H_3O^+ and H_2O is a stronger base (proton acceptor) than Cl^- and so the reaction is favoured in the forward direction

Weak acids

- Weak acids are those that only partially ionise in water
- E.g. In a solution of ethanoic acid, only a small portion of all the ethanoic acid molecules ionise to form hydrogen ions and ethanoate ions
 - $\text{CH}_3\text{COOH}_{(g)} \rightleftharpoons \text{H}^+_{(aq)} + \text{CH}_3\text{COO}^-_{(aq)}$
 $\text{CH}_3\text{COOH}_{(g)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{H}_3\text{O}^+_{(aq)} + \text{CH}_3\text{COO}^-_{(aq)}$
 - Double arrows are used to illustrate an equilibrium (i.e. the reverse reaction occurs to a significant extent)
 - Using the Brønsted-Lowry approach, H_3O^+ is a stronger acid (proton donor) than CH_3COOH and CH_3COO^- is a stronger base (proton acceptor) than H_2O and so the reaction is favoured in the reverse direction

Strong bases

- Strong bases are those that essentially completely dissociate to produce hydroxide ions in aqueous solution
- E.g. In a solution of sodium hydroxide, virtually the entire sodium hydroxide lattice has dissociated to form sodium and hydroxide ions
 - $\text{NaOH}_{(s)} \rightarrow \text{Na}^+_{(aq)} + \text{OH}^-_{(aq)}$
 - Because the equilibrium strongly favours the formation of products, a single arrow is used, showing only the forward reaction occurs
- All metal oxides and metal hydroxides virtually completely dissociate in solution, hence they are classified as strong bases

Weak bases

- Weak bases are those that only partially dissociate in water
- E.g. In a solution of ammonia, only a small portion of all the ammonia molecules react with water to form hydroxide and ammonium ions
 - $\text{NH}_3_{(aq)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{NH}_4^+_{(aq)} + \text{OH}^-_{(aq)}$
 - Double arrows are used to illustrate an equilibrium (i.e. the reverse reaction occurs to a significant extent)
 - Using the Brønsted-Lowry approach, OH^- is a stronger base (proton acceptor) than NH_3 and NH_4^+ is a stronger acid (proton donor) than H_2O and so the reaction is favoured in the reverse direction

Strong acids	Weak acids	Strong bases	Weak bases
nitric acid, HNO_3 sulfuric acid, H_2SO_4 hydrochloric acid, HCl hydrobromic acid, HBr hydroiodic acid, HI perchloric acid, HClO_4	acetic acid, CH_3COOH hydrofluoric acid, HF phosphoric acid, H_3PO_4 sulfurous acid, H_2SO_3 nitrous acid, HNO_2 hypochlorous acid, HClO carbonic acid, H_2CO_3 hydrogen cyanide, HCN hydrogen sulfide, H_2S lactic acid, $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$ citric acid, $\text{C}_6\text{H}_8\text{O}_7$ ammonium ion, NH_4^+ hydrogensulfate ion, HSO_4^-	metal hydroxides, e.g. sodium hydroxide, NaOH potassium hydroxide, KOH calcium hydroxide, $\text{Ca}(\text{OH})_2$	ammonia, NH_3 hydrogencarbonate ion, HCO_3^- carbonate ion, CO_3^{2-} sulfide ion, S^{2-} phosphate ion, PO_4^{3-} acetate ion, CH_3COO^- fluoride ion, F^-

Acidity Constants

- An acid ionisation constant (K_a) is a quantitative measure of the strength of an acid in solution. It is the equilibrium constant for a chemical reaction known as dissociation in the context of acid-base reactions
- In aqueous solution, the equilibrium of acid ionisation can be written symbolically as:

$$\text{HA}_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})} \rightleftharpoons \text{A}^-_{(\text{aq})} + \text{H}_3\text{O}^+_{(\text{aq})}$$
- The chemical species HA , A^- and H_3O^+ are said to be in equilibrium when their concentrations do not change with the passing of time
- The dissociation constant is usually written as a quotient of the equilibrium concentrations (in mol L^{-1}) as follows:

$$K_a = \frac{[\text{A}^-][\text{H}_3\text{O}^+]}{[\text{HA}]}$$
 - o Strong acids ionise completely in water, hence K_a is large
 - o Weak acids only ionise partially in water, hence K_a is small
- Acid dissociation constants only apply when the acid is dissolved in water, and are usually quoted at 25°C

Monoprotic and Polyprotic Acids

- Acids such as hydrochloric acid HCl, nitric acid HNO₃, and acetic acid CH₃COOH, are monoprotic acids because each molecule of the acid produces only one hydrogen ion during the ionisation process in aqueous solution
- Some acids such as sulfuric acid, H₂SO₄, and phosphoric acid, H₃PO₄, produce more than one hydrogen ion when they dissolve in water. These acids are known as polyprotic or multiprotic acids
 - o Sulfuric acid is an example of a **diprotic** acid because it has two hydrogen ions it can lose or donate in a reaction with a base
 - It is a strong acid, and so in water it completely loses its 'first' hydrogen ion:

$$\text{H}_2\text{SO}_4(\text{l}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{HSO}_4^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$$
 - The hydrogensulfate ion formed in this reaction then acts as a weak acid resulting in the loss of the 'second' hydrogen ion

$$\text{HSO}_4^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{SO}_4^{2-}(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$$
 - o Phosphoric acid is a **triprotic** acid because it has three hydrogen ions it can lose or donate in a reaction with a base
 - In water, the following progressive ionisations occur:

$$\text{H}_3\text{PO}_4(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_2\text{PO}_4^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$$

$$\text{H}_2\text{PO}_4^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HPO}_4^{2-}(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$$

$$\text{HPO}_4^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{PO}_4^{3-}(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$$
 - Phosphoric acid is a weak acid, H₂PO₄⁻ is a weaker acid and, in turn, HPO₄²⁻ is an even weaker acid
 - I.e. The first ionisation reaction occurs to a greater extent than does the second reaction, which occurs to a greater extent than the third reaction
 - o I.e. $K_{a1} > K_{a2} > K_{a3}$

Self-ionisation of Water

- Water is a weak electrolyte, and to a very small extent undergoes auto- or self-ionisation:
 - o $2\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq})$
 - o $\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq})$
- The first equation represents the Brønsted-Lowry approach
 - o One water molecule is acting as the proton donor, while the other is accepting the proton
 - A substance that is able to both react as an acid and a base in the same reaction is called an **amphoteric** substance
- The second simplified equation indicates that water ionises to produce some aquated hydrogen and hydroxide ions
- Both equations indicate that equal amounts of acid and base are produced
- In the ionisation of water, equilibrium strongly favours the reactants (i.e. reverse reaction is favoured)
 - o This means that only small concentrations of hydrogen ions and hydroxide ions are formed and most of the water remains as unionised water molecules
 - o The equilibrium constant for the ionisation of water is given by:

$$K_W = [\text{H}^+][\text{OH}^-]$$
 - o K_W is called the ionisation constant for water, and as with an equilibrium constant, it depends on the temperature. Its value at 25°C is 1.0×10^{-14}

- This means that for any aqueous solution at 25°C, the product of the hydrogen ion and hydroxide ion concentrations is always 1.0×10^{-14}
 - In pure water, or any neutral solution: $[H^+] = [OH^-] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7} \text{ mol L}^{-1}$
 - In acidic solutions: $[H^+] > 1.0 \times 10^{-7} \text{ mol L}^{-1} > [OH^-]$
 - In basic solutions: $[H^+] < 1.0 \times 10^{-7} \text{ mol L}^{-1} < [OH^-]$

The pH Acidity Scale

- Although the hydrogen ion and hydroxide ion concentrations are valid ways of expressing the acidity or basicity of aqueous solutions, they are somewhat cumbersome because they involve the use of indices
 - The more convenient method of indicating acidity/basicity is the pH scale
- pH is defined by the formula:
 - $\text{pH} = -\log_{10}[H^+]$
 $= -\log_{10} \frac{1.0 \times 10^{-14}}{[OH^-]}$ This formula uses K_W to find the pH when $[OH^-]$ is known
 - $[H^+] = 10^{-\text{pH}}$
- The pH of water or a neutral solution at 25°C is 7.0
 - The pH of an acidic solution at 25°C < 7.0
 - The pH of a basic solution at 25°C > 7.0
- The following aspects of the pH scale should be noted:
 - As the $[H^+]$ increases, pH decreases
 - The greater the pH, the greater the acidity of the solution
 - A change of one pH unit represents a tenfold change in hydrogen ion concentration
 - The range of pH values are from a little below -1 to slightly above 15
 - However, for most solutions of acids and bases the range of values is from 0 to 14

The Effect of Temperature on the pH of Pure Water

- The pH scale was demonstrated by using the K_W of water at 25°C. This exemplifies that pure water does not always have a pH of 7 because, as with all equilibrium reactions, the K_W value changes with temperature
- The forward reaction in the equilibrium $2H_2O(l) \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$ is endothermic
 - Thus the forward reaction is favoured when the temperature is increased
 - Thus an increase in temperature increases the K_W value as $[H^+]$ and $[OH^-]$ increase
 - Thus at a temperature other than 25°C, $\text{pH} = -\log_{10}[H^+] \neq 7$
- This shows that a more robust definition is required for a neutral solution. A neutral solution is neutral when $[H^+] = [OH^-]$
 - Thus pure water is neutral at all temperatures but the pH varies with temperature

Calculating pH Following Mixing of a Strong Acid and Strong Base

- When a solution of a strong acid reacts completely with a solution of a strong base in the stoichiometric amounts required by the balanced equation, the resulting solution is neutral (i.e. $[H^+] = [OH^-]$) and so the pH is 7 (at 25°C)
- If the strong acid and strong base are not mixed in stoichiometric amounts, then some of either the acid or the base will remain unreacted after the reaction. This remaining acid or base that will determine the pH of the final solution
 - o One must remember to add the volume of the new solutions when calculating the concentration of excess H^+ or OH^-

The pH of Salts

- Salts are ionic compounds produced after the reaction of an acid and a base
 - o This implies that a salt is an ionic compound containing a cation other than H^+ and an anion other than OH^- and O^{2-}
- In dilute aqueous solutions, salts are completely dissociated into ions because they are strong electrolytes. These solutions may then be acidic, neutral or basic, depending on the particular ions in the salt (i.e. the dissociated cation and/or anions may then react with water)
 - o The reaction with water is called a hydrolysis reaction
- In order to predict the acid-base nature of a salt, it is necessary to consider the acid-base properties of the individual ions making up the salt
- The acid-base properties of cations and anions are summarised in the table below:

Neutral ions	Ions that form acidic solutions	Ions that form basic solutions
Group 1 and 2 ions, e.g. Na^+ , K^+ , Ca^{2+} , Mg^{2+}	Conjugate positive ions of weak bases, e.g. NH_4^+	Conjugate negative ions of weak acids, e.g. CH_3COO^- , F^- , CN^-
Conjugate negative ions of strong acids, e.g. Cl^- , Br^- , NO_3^-	Group 13 and transition metal ions, e.g. Al^{3+} , Fe^{3+}	HCO_3^- and CO_3^{2-}
SO_4^{2-}	HSO_4^-	HPO_4^{2-} and PO_4^{3-}
	$H_2PO_4^-$	

Neutral ions

- Anions that are derived from (i.e. conjugate ions of) strong acids
 - o Anions such as Cl^- have no tendency to react with water to form HCl and hydroxide ion (as they have negligible base strength), and thus are neutral in solution
- Group I and II cations
 - o These cations are derived from strong bases such as sodium hydroxide and magnesium oxide (and thus have negligible acid strength), and thus are neutral in solution

Acidic ions

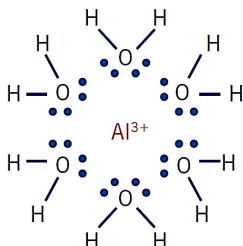
- Cations that are derived from weak bases
 - o The conjugate cation of a weak base is acidic. Consequently, the positive ion undergoes hydrolysis to form hydronium ions in solution, and thus is acidic in solution
 - E.g. The ammonium ion (the conjugate pair of the weak base ammonia), will participate in the following equilibrium: $NH_4^+_{(aq)} + H_2O_{(l)} \rightleftharpoons NH_3_{(aq)} + H_3O^+_{(aq)}$

- Cations that are derived from aquated metal ions

- The +3 ions formed from metals in group 13 of the periodic table, as well as many of the +2 and +3 ions of the transition metals, produce salts that are acidic

- The reason for this is that these small, highly charged ions attract water molecules to themselves to form a hydrated ion via ion-dipole forces

- E.g. An aluminium ion has six water molecules attached to it by ion-dipole bonds



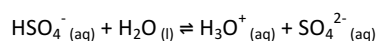
- The hydrated metal ion can then act as a Brønsted-Lowry acid and donate a hydrogen ion from one of the water molecules attracted to it, to another water molecule in the solution, and thus is acidic in solution

- E.g. $[\text{Al}(\text{H}_2\text{O})_6]^{3+}_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})} \rightleftharpoons [\text{Al}(\text{H}_2\text{O})_5(\text{OH})]^{2+}_{(\text{aq})} + \text{H}_3\text{O}^{+}_{(\text{aq})}$

- Certain anions are derived from polyprotic acids

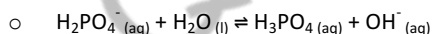
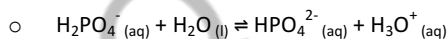
- E.g. The hydrogensulfate ion (HSO_4^-) is derived from sulfuric acid

- Solutions containing the hydrogensulfate ion are acidic due to the following hydrolysis reaction:



- However, anions that contain acidic hydrogen atoms and are derived from polyprotic acids are able to undergo separate hydrolysis reactions that produce either H^+ and OH^- in solution

- E.g. The dihydrogenphosphate ion (H_2PO_4^-) can react with water in two ways:



- These are competing hydrolysis reactions. Whether the anion exhibits acidic or basic properties in solution depends on the relative tendencies of these competing hydrolysis reaction
- In this case H_2PO_4^- is an acidic anion because it is a better proton donor than proton acceptor

- It must be memorised that HSO_4^- and H_2PO_4^- are better proton donors than proton acceptors, and thus are acidic in solution

Basic ions

- Basic anions that are derived from weak acids

- The conjugate anion of a weak acid is basic. Consequently, the negative ion undergoes hydrolysis to form hydronium ions in solution, and thus is basic in solution

- E.g. The ethanoate ion (the conjugate pair of the weak ethanoic acid), will participate in the following equilibrium: $\text{CH}_3\text{COO}^{-}_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})} \rightleftharpoons \text{CH}_3\text{COOH}_{(\text{aq})} + \text{OH}^{-}_{(\text{aq})}$

- Certain anions are derived from polyprotic acids. As discussed earlier, polyprotic acids undergo competing hydrolysis reactions

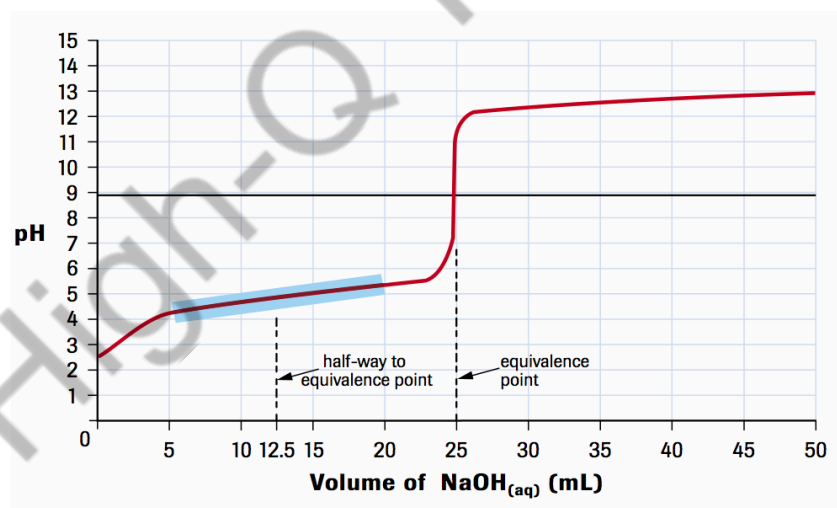
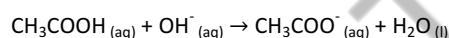
- It must be memorised that the following ions (derived from polyprotic acids) are better proton acceptors than proton donors, and thus produce basic solutions when dissolved in water:

- HCO_3^-
- HPO_4^{2-}

- To determine whether a particular salt will undergo hydrolysis to form an acidic or basic solution, it is necessary to consider the cation and anion concerned
 - o E.g. A NaCl solution will be neutral as both Na^+ and Cl^- are neutral ions
 - o E.g. In solutions of KCH_3COO and Na_2S , the CH_3COO^- and S^{2-} ions react with water to produce small amounts of hydroxide ions, and so basic solutions result
 - o E.g. In solutions of NH_4Cl and $\text{Fe}(\text{NO}_3)_3$, the NH_4^+ and $[\text{Fe}(\text{H}_2\text{O}_6)]^{3+}$ ions react with water to produce small amounts of hydronium ions, and so acidic solutions result

Buffers

- Buffer solutions are those that resist a large changes in pH when proportionally small quantities of an acid or a base are added to it
- There are two ways of producing a buffer:
 - o Mixing a weak acid or a base with its conjugate pair
 - E.g. A weak acid such as ethanoic acid is mixed with a soluble salt of its conjugate base, such as sodium ethanoate
 - E.g. A weak base such as ammonia is mixed with a soluble salt of its conjugate acid, such as ammonium chloride
 - o A titration process
 - E.g. In the titration of ethanoic acid with sodium hydroxide (as shown in the graph below)



- When a volume of 12.5 mL of sodium hydroxide has been added, the solution is half-way to equivalence point
 - o Since half of the equivalence volume has been added, half of the original ethanoic acid has reacted to produce ethanoate ions
 - o Therefore, the mixture in this buffering region contains approximately equal amounts of the unreacted weak acid, $\text{CH}_3\text{COOH}_{(\text{aq})}$, and its conjugate base, $\text{CH}_3\text{COO}^-_{(\text{aq})}$, produced in the reaction

Buffering action

- A buffer, by definition has the ability to maintain a nearly constant pH when small amounts of acid or base is added
- Buffering action can be explained using the principles of chemical equilibrium (e.g. Le Châtelier's principle)
 - o E.g. Consider a buffer system composed of ethanoic acid and ethanoate ions
 - When a small amount of base (e.g. NaOH) is added to the buffer, the hydroxide ion concentration increases instantaneously. The system responds by shifting the equilibrium to favour the forward reaction
 - This partially counteracts the imposed change (i.e. increased hydroxide ion concentration), and thus there is only a small increase in pH
 - This buffer would work equally well if a small amount of an acid (e.g. HCl) is added to the buffer. The hydroxide ions are consumed by the hydrogen ions, and so the equilibrium shifts so that the mixture now has a slightly higher ratio of ethanoic acid to ethanoate ions and a slightly less decrease in pH than it would have had if there were no buffer present

Buffering capacity

- o The extent to which the buffer can 'absorb' the extra acid or base added is called the buffer capacity. The buffer capacity depends on the concentrations of the weak acid and its conjugate base
 - The greater the concentration of the conjugate pair, the greater the amount of acid or base that can be added without depleting the buffer's capacity to maintain a constant pH
- o Consider a buffer solution consisting of a mixture of the weak acid HA and its conjugate base A⁻ in which the following equilibrium exists:

$$\text{HA}_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})} \rightleftharpoons \text{A}^{-}_{(\text{aq})} + \text{H}_3\text{O}^{+}_{(\text{aq})}$$
- o While the ratio of [HA]/[A⁻] influences the pH of a solution, the actual concentrations of HA and A⁻ influence the effectiveness of a buffer. The more HA molecules and A⁻ ions there are available, addition of a strong acid or base will have a lesser effect on the pH of a system
 - Consider the addition of a strong acid such as HCl to the buffer solution
 - Initially, the HCl donates its proton to the weak base (A⁻) through the reaction $\text{A}^{-} + \text{HCl} \rightarrow \text{HA} + \text{Cl}^{-}$
 - As long as there is an adequate source of A⁻ present, the change in pH will be small
 - If we keep adding HCl, the weak base A⁻ will eventually be consumed. Once the A⁻ is depleted, any additional HCl will donate its proton to water through the reaction $\text{HCl} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^{+} + \text{Cl}^{-}$
 - This will dramatically increase the concentration [H⁺] and so the change in pH will be marked